

# Liquid-liquid phase transition in Stillinger-Weber silicon

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## Abstract.

It was recently demonstrated that the Stillinger-Weber silicon undergoes a liquid-liquid first-order phase transition deep into the supercooled region (Sastry and Angell, *Nature Materials* 2, 739 (2003)). Here we study the effects of perturbations on this phase transition. We show that the order of the liquid-liquid transition changes with negative pressure. We also find that the liquid-liquid transition disappears when the three-body term of the potential is strengthened by as little as 5 %. This implies that the details of the potential could affect strongly the nature and even the existence of the liquid-liquid phase.

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## 1. Introduction

The amorphous phase of Si is particular in that it does not correspond to the arrested liquid phase, contrarily to glasses: while liquid Si is metallic, with an average coordination around 6.4 at ambient conditions [41, 42, 20],  $\alpha$ -Si has a coordination near 4 and is a semiconductor. The existence of a possible intermediate phase, explaining in part this difference, was first suggested by Aptekar, who showed that the Gibbs free energy of the amorphous phase does not extrapolate smoothly to that of the liquid, indicating that an additional phase transition should occur at around 1450 K [9]. Much experimental [8, 18, 39, 11] and numerical work [4, 7, 29, 28] followed, supporting the existence of such an additional phase, long thought to be the amorphous phase.

A breakthrough in the understanding of this unusual feature came a few years ago with the first clear experimental evidence for liquid polymorphism in a number of materials such as  $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$  [1]. The distinct liquid-phases hypothesis was first formulated to explain several properties of water near the melting temperature, including the density anomalies, and was supported by the polymorphism of the crystal and amorphous phases. More precisely, Mishima *et al.* [30, 31] proposed that the liquid-liquid transition for water between a low density liquid (LDL) and a high density liquid (HDL) is the continuity at higher temperatures of the known amorphous phase transition between the low and high density forms.

In analogy with water, it was rapidly suggested that a “fragile-to-strong” liquid transition occurs in the supercooled regime of silicon, the resulting viscous liquid at low temperature (i.e. LDL) corresponding to the precursor phase of the amorphous metastable state [5, 6, 7]; the best candidates for such a liquid-liquid phase transition are tetravalent systems, which display an open molecular structure, such as  $\text{H}_2\text{O}$ , C, Si, Ge,  $\text{SiO}_2$  and  $\text{GeO}_2$  which all show a density maximum in function of temperature [34, 37, 35]. *Ab initio* numerical calculations [19] also show a transition between a low (LDA) and high (HDA) density amorphous phase of silicon under high pressure, providing an additional support for this hypothesis. More importantly, the liquid-liquid transition for silicon is not excluded from the stable region of the phase diagram and recent experimental work on liquids revealed a structural change for liquid Si [22],  $\text{GeO}_2$  [33] and P [25] under high pressure.

Recently, the first clear demonstration of the existence of this low-density liquid phase, at least for the Stillinger-Weber silicon, was given by Sastry and Angell [36]. In this elegant work, Sastry and Angell identify a first-order liquid-liquid phase transition taking place around 1060 K by measure the heat release in a simulation in the NPH ensemble, finding results in agreement with a number of previous simulations. They showed, moreover, that the resulting phase is a very viscous tetrahedral liquid which should be the precursor to the well-characterized amorphous phase.

Although this pioneering work establishes the existence of the liquid-liquid phase transition, it is essential to characterize the behavior of this transition under perturbations. In this Paper, we study the impact of pressure and potential

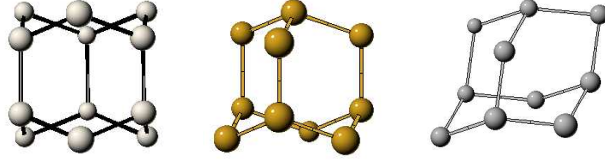
modifications on this transition. In particular, we find that the amorphous phase does correspond to the glassy low-density liquid at zero pressure. However, we also find that the liquid-liquid transition changes order with negative pressure. We show that this transition becomes unreachable with a very slight change of the SW potential, indicating that while this transition is clearly present for this potential, it remains to be fully demonstrated for real Si.

## 2. Methods

The molecular dynamical simulations for this work are performed in three ensembles: isobaric (NPE), isothermal-isobaric (NPT) and iso-enthalpic-isobaric (NPH). All simulations are done at  $P=0$  in a cubic box containing 1000 atoms, with periodic-boundary conditions. The extended-system method of Andersen is used to control pressure [3, 23, 16] and Hoover's constraint method for the temperature [24, 21, 2]. We use the fifth-order Gear predictor-corrector to integrate Newton's equation with a time step  $\Delta t = 1.15$  fs. Typically, after a change in temperature, the simulations are equilibrated for 50 000  $\Delta t$  (58 ps) and statistics are accumulated over 450 000  $\Delta t$  (518 ps).

Atomic interactions are represented by the Stillinger-Weber potential (SW), developed to reproduce accurately the crystalline and the liquid state of Si [38]. Although this potential has known limitations, especially in the amorphous phase [28, 29, 13, 40], it ensures a reasonable description of the liquid phase [17, 12, 15]. Its melting temperature is also near the experimental value of 1683 K [10]: averaging temperature of a box with a crystal-liquid interface at equilibrium, we find a temperature of  $1662 \pm 1$  K, in agreement with  $T_m = 1665$  K found by Landman *et al.* [27] using a similar method.

To measure directly the degree of local crystallinity in the liquid and amorphous phases, we use a set of criteria that identify the smallest three-dimensional structures associated with wurtzite, diamond and  $\beta$ -tin crystalline structures (see Fig. 1). We restrict this topological analysis to pairs of atoms that are within 2.75 Å of each other to ensure that these atoms are close to a crystalline or amorphous environment; for all others quantities, we consider the first-neighbor cut-off to be at the first minimum between the first- and second-neighbor peaks in the radial distribution function (RDF). The wurtzite elementary block is a 12-atom cluster with two six-fold rings stacked on top of each other and connected by three bonds; the elementary building block for both diamond and  $\beta$ -tin has the same topology consisting of four six-membered rings placed back to back, forming a 10-atom cluster. These elementary clusters are only present with a low density in good quality amorphous Si relaxed with SW (10 to 20 at.%) as well as in the HDL (5-10 at.%) providing a very convenient measure of local crystalline order; they were used for the same purpose in a previous study of crystallization [32]. This order parameter is a much more sensitive measure of crystallinity than the structure factor or the RDF.



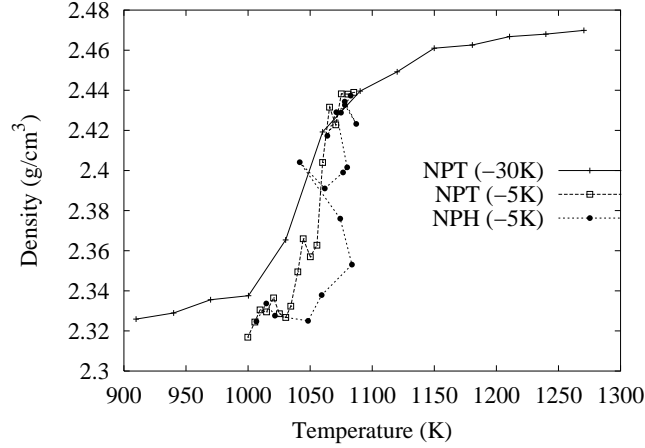
**Figure 1.** The three basic building blocks which represent the order parameter for characterizing the state of crystallization of the model. The wurtzite basic block (left) is a 12-atom cluster composed of two sixfold rings whereas the diamond basic block (center) is a 10-atom cluster with four sixfold rings. The  $\beta$ -tin basic block (right) is equal to a diamond basic block where the tetrahedra are compressed in one direction and elongated along the two others axes.

### 3. Results

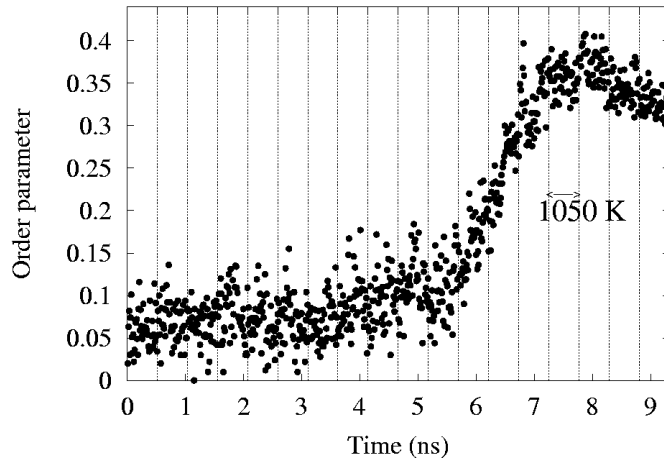
#### 3.1. Liquid-liquid transition

*3.1.1. Zero pressure* The Stillinger-Weber liquid-to-amorphous transition was one of the first problems studied after the potential was introduced. Broughton and Li observed that supercooled silicon transforms continuously into a glass at low temperature [15]. Further investigations by Luedtke and Landman, however, showed that the liquid undergoes a first-order phase transition at around 1060 K, transforming directly into a reasonably good quality amorphous solid if the simulated cooling down is slow enough [28, 29]. This phase was found to be reversible as the system is heated from the amorphous phase. Following recent work on polymorphism in liquids, Angell and Borick [4] suggested that the phase just below the transition temperature is not an amorphous solid but a very viscous liquid, freezing into the amorphous phase. As discussed in the introduction, this suggestion was recently demonstrated by Sastry and Angell using an elegant analysis [36]: simulating undercooling of *l*-Si in the NPH ensemble, it is possible to show unequivocally that the system undergoes a first order liquid-liquid transition from a high density liquid (HDL) to a low density liquid (LDL) before transforming continuously to the amorphous state, a thermodynamically metastable state.

Our simulations find the same first-order liquid-liquid phase transition near 1060 K as the system is cooled slowly from high temperature. Figure 2 shows the density as a function of the temperature in the NPT ensemble with steps of -30 and -5 K between each point while the NPH data is obtained with steps of -5 K. Small temperature steps are needed to notice the details of the first-order liquid-liquid transition. Each of these points is obtained by averaging over 450 000 time steps, after a 50 000 time step equilibration period. As explained in Ref. [36], the discontinuities in the NPH curve are associated with a first-order transition. The transition is also clearly visible in the density: the system expands brutally as it is cooled from 1090 to 1050 K and its density falls from 2.44 to 2.32 g/cm<sup>3</sup>. This change in volume is associated with a lowering of coordination from 4.9 to 4.24 as the system becomes more like a network liquid.



**Figure 2.** Mean density as a function of temperature for a 1000-atom SW cell at zero pressure. Simulations start with a well-equilibrated model of *l*-Si at 1300 and 1090 K for temperature steps of -30 and -5 K respectively. The first two simulations are performed in the NPT ensemble, with the temperature lowered by steps of 30 K (crosses and solid line) and 5 K (open squares and dashed line) while the last curve shows the density as a function of temperature for a simulation in the NPH ensemble in which the temperature is decreased by steps of 5 K (filled circles and dotted line). Lines are guide to the eye.



**Figure 3.** Evolution of the proportion of atoms in crystalline structures for the simulation in the NPH ensemble at zero pressure. Each section represents a time interval at a given enthalpy with the kinetic energy reduced by 5 K at the end of each interval. Each interval correspond to a thermodynamic point on the density vs temperature figure (see Fig. 2). The double arrow indicated time interval for which the average temperature is 1050 K.

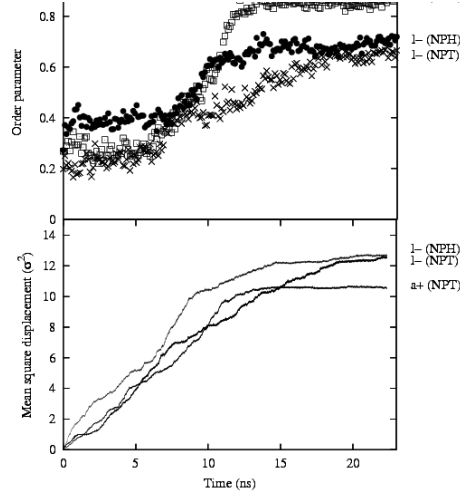
The LDL possesses a largely tetrahedral structure with a coordination of 4.24 at 1050 K in NPH ensemble, near the 4.2 value reported by Sastry and Angell [36]. The topological analysis, using the elementary blocks, shows that 37 % of the atoms are associated with a basic building block; the structure is partially crystallized (Fig. 3) whereas the HDL phase at  $T = 1090$  K contains only 5-10 at.% of elementary blocks. The diffusion of atoms changes abruptly during the transition and the diffusivity of the quenched liquids at 1050 K is  $3.2 \cdot 10^{-8}$  and  $3.8 \cdot 10^{-7}$  cm<sup>2</sup>/s in NPH and NPT ensembles, respectively, corresponding to a very viscous liquid.

We verify that the LDL phase is the liquid counterpart to amorphous silicon. To check this, we heated slowly a high-quality amorphous model generated by a bond-switching technique described in Ref. [14] and relaxed with the SW potential, and compared with the LDL system. The amorphous phase is stable and does not crystallize after a long simulation (20 ns) at 1000 K. Its diffusivity increases rapidly at 1050K, however, and it reaches a value very similar to that of the LDL at the same temperature, crystallizing within 12 ns (with 80 at.% of elementary blocks). This nucleation time is similar to that observed in the LDL obtained by cooling in the NPT and NPH ensemble (see Fig. 4). The degree of crystallization in Fig. 4 (top) after 20 ns seems to be closely related to the quality of the network in the initial state, as defined by its coordination. The amorphous model, with an initial coordination 4, crystallizes to 84% while only 66 and 71 % of atoms belong to basic block structures for the liquids cooled in the NPT and NPH ensemble, with an average coordination of 4.41 and 4.24 respectively.

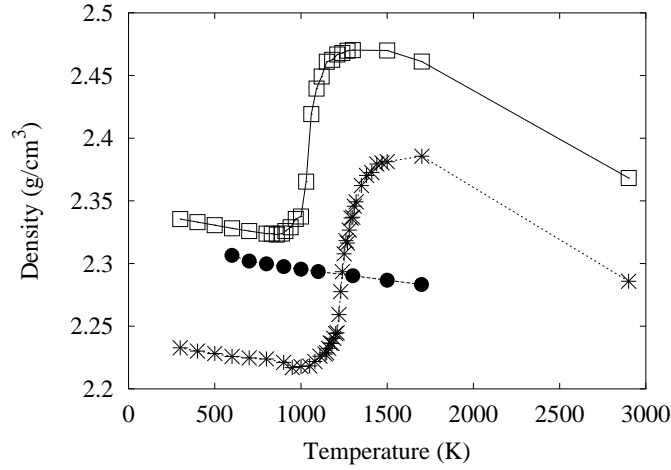
Since the phase transition is buried deeply into the supercooled region, it is difficult to reverse the transition and go from LDL to HDL. Heated by step from 1050 K, the LDL phase remains stable until it crystallizes at around 1150 K, showing considerable hysteresis. In order to reach HDL, it is necessary to bring the LDL system at once from 1050 to 1250 K, a behavior already noticed by Broughton and Li [15]. The HDL phase, on the contrary, is stable against crystallization and does not show any significant density of elementary crystalline blocks even after 20 ns of simulation at a temperature as low as 1100 K.

*3.1.2. Negative pressure* As discussed in the previous section, the LDL phase of the SW potential shows an average coordination of 4.24 at 1050 K, indicating the presence of a large fraction of mostly 5-fold coordinated atoms. This coordination is significantly higher than the experimental measurement, which shows an average coordination of 3.88 [26], and than the theoretically accepted value of 4.0 [13, 40, 14]. Such discrepancy is largely due to the limits of the potential. As discussed in Ref. [13], for example, the SW potential systematically produces an over-coordinated amorphous phase; even very slow cooling fails to produce configurations near an average coordination of 4.0 [29].

Because of this discrepancy, it is important to test the stability of the LDL phase as the system is biased towards obtaining a higher-quality amorphous phase. It is possible to favor the formation of a lower-coordinated liquid by applying a negative pressure on the system or by changing the potential. In this section, we study the HDL to LDL



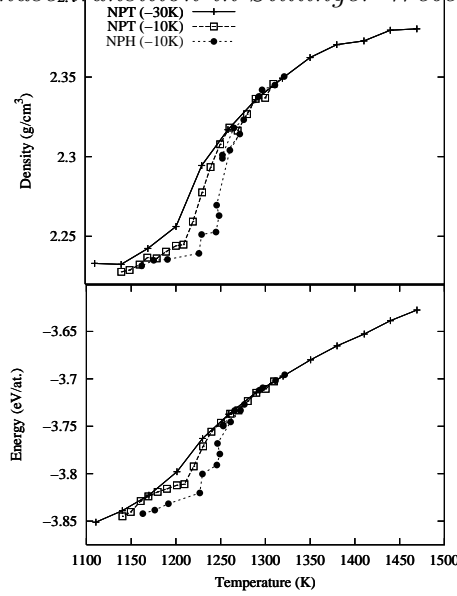
**Figure 4.** Proportion of atoms belonging to basic building-block structures (top) and mean square displacement per atoms (bottom) for simulation performed at a constant temperature ( $T = 1050$  K). The initial liquid configurations at 1050 K are obtained from the cooling simulations in the NPT "l- (NPT)" and NPH "l- (NPH)" ensemble and are run in the same ensemble. The initial amorphous model was obtained by heating to 1050 K in the NPT ensemble "a+ (NPT)".



**Figure 5.** Density dependence of temperature for liquid and crystalline silicon. We show the results for the crystal ( $\bullet$ ) and liquid at zero GPa ( $\square$ ) and -2 GPa ( $*$ ). At zero pressure, the supercooled liquid undergoes a first order transition at around 1060 K. Lines are a guide to the eyes.

at a negative pressure of -2 GPa, near to the stability limit of the liquid; effects of a potential change are studied in the next section.

To first order, the application of negative pressure simply shifts the phase diagram (Fig. 5), as the density maximum moves from 1300 K to 1700 K and the liquid-liquid transition from 1060 K to 1250 K, in agreement with the isochoric cooling curves as a



**Figure 6.** Mean density (top) and energy (bottom) as a function of temperature for a system maintained at a negative pressure of -2 GPa. The crosses (solid line) show the results of a NPT simulation starting from a well-relaxed liquid configuration at 1500 K and then gradually lowered by steps of 30 K. The open squares (dashed line) and the filled circles (dotted line) correspond, respectively, to simulations in the NPT and NPH ensemble with an initial liquid configuration equilibrated at 1340 K where the temperature is lowered by steps of 10 K. Lines are guide to the eye.

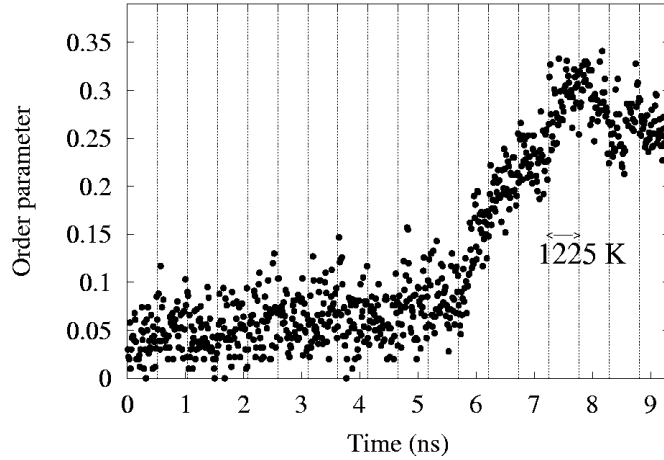
function of density presented by Angell *et al.* [7].

Similarly, the HDL to LDL transition remains at negative pressure. However, the system does not emit latent heat during the transition and NPH simulations, with cooling steps of 10 K, closely follow the NPT curve (see Fig. 6). The HDL transforms, therefore, via a second-order phase transition into a lower-density phase. During the transition, between 1270 and 1225 K, the system transforms in a tetravalent structure with the average coordination falling from 4.95 to 4.18 in NPH conditions and the proportion of atoms in crystalline structures increases from 5 % to 30 %. At 1225 K, the diffusivity of the LDL is  $1.6 \cdot 10^{-7} \text{ cm}^2/\text{s}$ , and is therefore still a liquid.

The theoretical model of Aptekar [9] locates the liquid-liquid transition at around 1500 K for Si at zero pressure and predicts a second critical point that terminates the first-order transition at -1.5 GPa in the supercooled liquid region. At -2 GPa, this model should therefore be below the critical point. Our picture is more complex as there is now a second-order phase transition between the HDL and LDL, indicating that critical point does not correspond to the end of a coexistence line.

**3.1.3. Modified potential** High-quality amorphous structures require a significant strengthening of the three-body term of the SW potential; an increase of 50 % is necessary to ensure a coordination of 4 in the amorphous phase for this potential [40, 28, 15]. This strong modification of the potential, however, completely changes the phase diagram of the system, removing the maximum in the density of the liquid phase and



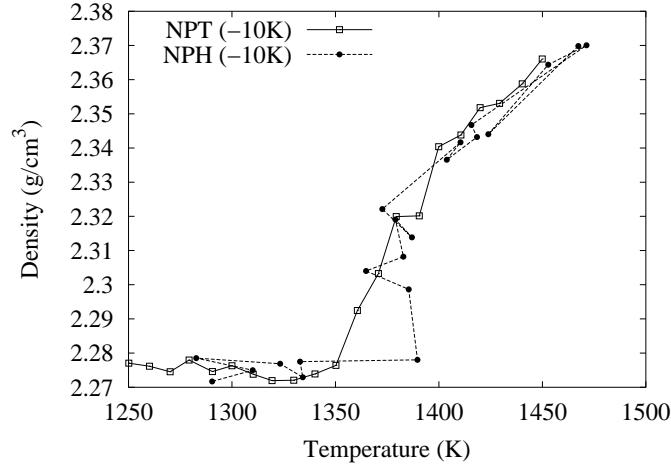


**Figure 7.** Evolution of the proportion of atoms in crystalline structures for the simulation in NPH ensemble at a negative pressure of -2 GPa. Each section represents a time interval at a given enthalpy with the kinetic energy reduced by 5 K at the end of each interval. Each interval correspond to a thermodynamic point on the density vs temperature figure (see Fig. 6). The double arrow indicated time interval for which the average temperature is 1225 K.

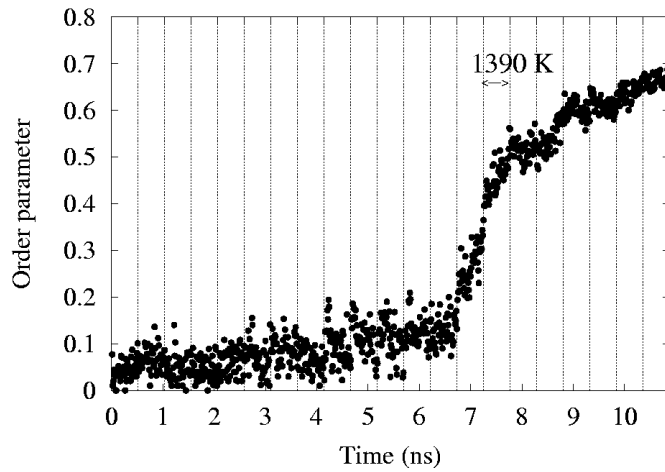
setting a lower density to the liquid than the crystal. Although a 12.5 % modification to the three-body term restores a temperature of density maximum in the liquid phase, the amorphous (or glassy) state reaches a lower density than the crystal. Thus, in order to preserve the main features of the SW phase diagram, we use much weaker modification, increasing the three-body term by 5 %, in order to verify the universality of the liquid-liquid phase transition.

The transition from the high to low density phase has features similar to that for the original SW potential. In particular, a net release of latent heat confirms that the transition is first order. However, the small strengthening of the three-body term augments significantly the nucleation rate of Si and raises the transition temperature from 1060 K to 1390 K (Fig. 9), indicating that the transition is qualitatively different. Indeed, the new phase, obtained following either the NPT or the NPH conditions, is already considerably crystalline at the transition: local-order analysis shows that the NPH configuration at 1390 K and 2.28 g/cm<sup>3</sup> occurring during the transition is crystallizing, with 55 % of all atoms belonging to crystalline structures. The liquid-liquid transition is therefore totally hidden by the crystallization.

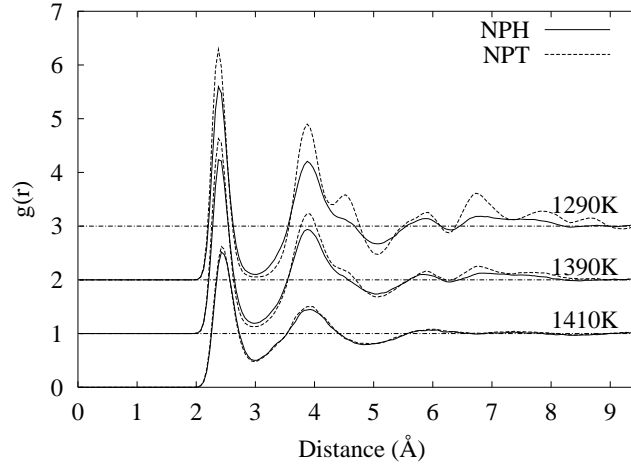
Because of the crystallization, the NPH and NPT simulations do not finish in the same thermodynamical state after the transition, contrarily to what is observed with the original SW potential: the NPT simulation shows a much more rapid crystallization than the NPH and at 1290 K, more than 95 % of all atoms are in a crystalline environment against 67 % for the NPH simulation. This high degree of crystallinity can be seen directly in the RDF, as shown in Fig. 10: at 1390 K, only the NPT simulation shows



**Figure 8.** Density as a function of temperature with the modified SW potential ( $\lambda = 1.05\lambda_0$ ). The open squares (solid line) and the filled circles (dashed line) show the result of simulation in the NPT and NPH ensemble, respectively, with cooling by steps of 10 K starting from an equilibrated *l*-Si configuration at 1460 K. Lines are guide to the eye.



**Figure 9.** Evolution of the proportion of atoms in crystalline structures for a simulation in the NPH ensemble with the modified SW potential. Each section represents a time interval at a given enthalpy with the kinetic energy reduced by 5 K at the end of each interval. Each interval correspond to a thermodynamic point on the density vs temperature figure (see Fig. 9). The double arrow indicated time interval for which the average temperature is 1390 K.



**Figure 10.** Radial distribution function of the modified SW potential near the transition temperature in the NPT and NPH ensemble. The RDF are measure at different temperatures: 1290 K (top), 1390 (middle) and 1410 K (bottom).

the third-neighbor peak, while it is visible also in the NPH simulation at 1290 K.

#### 4. Discussion and conclusion

The liquid-liquid transition in Si is difficult to observe because it should occur deep in the undercooled region of the phase diagram. It is not clear whether this part of the phase diagram can be reached experimentally, so we must rely on simulations to characterize this important phenomenon. Even with the fast cooling accessible to molecular dynamics, the temperature window for observing the LDL is very narrow and the viscosity increases rapidly as the LDL becomes glassy  $\alpha$ -Si. This difficulty explains why the phase was only demonstrated recently for SW Si.

At zero pressure, Sastry and Angell [36] demonstrated clearly the existence of a liquid-liquid phase transition in the SW Si. Moreover, we could verify that the amorphous phase, obtained via an independent method, does correspond to the LDL, as was suggested previously.

The question remains as to whether the LDL phase also exists in the real material. By moving around this thermodynamical point, it is possible to verify the stability of this result and whether or not this phase is likely to occur in Si.

As one of the main limitations of the SW potential is that it cannot describe properly the structure of the amorphous phase, corresponding to the glassy phase of LDL, we look at the impact of getting a better coordinated  $\alpha$ -Si on the phase diagram by applying a negative pressure and changing slightly the potential.

Following the analysis of Aptekar, a critical point should exist at the end of the coexistence line below -1.5 GPa [9]. We find instead that the order of the liquid-liquid transition changes from first to second, with an absence of heat release during the transition. The relative change in structure from HDL to LDL is very similar to

that obtained at zero pressure, however, and the average coordination is closer to 4.0. Nevertheless, the LDL seems to be even more unstable under crystallization than at zero pressure.

It is also possible to favor a lower coordination in the amorphous phase by increasing the strength of the three-body force of the SW potential. To keep the same overall phase diagram, we modify this term only very slightly, increasing it by only 5 %. The impact of this modification is surprisingly important: the first-order transition move from 1060 to 1390 K and changes in character, crystallization occurs almost immediately and there is no trace of a low-density liquid. The temperature shift is much larger than the change in melting temperature, which is about 20 K, suggesting that the transition seen with the strengthened potential is the standard crystallization transition in the undercooled phase. The liquid-liquid transition, if present, is therefore not easily reachable even on MD timescale. This is particularly clear using a topological order-parameter which identifies the degree of crystallinity with much more precision than averaged structural quantities such as the structure factor and the RDF.

While the results of Sastry and Angell provided the first clear demonstration of the existence of a liquid-liquid first-order transition in SW Si [36], our results suggest that the existence and the nature of the liquid-liquid phase transition in real Si must be confirmed through further simulations with a wider set of potentials and, if possible, through experiment.

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